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(54) Title: FLAME RETARDANT POLYMER FORMULATION (57) Abstract <p>The invention describes a formulation for halogenated polymers containing a synergistic mix of flame retardants comprising 10-400 phr of an aluminium or magnesium hydroxide and 0.5-80 phr of tin oxide or a metal stannate or hydroxystannate.</p>		

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FLAME RETARDANT POLYMER FORMULATION

It is estimated that in excess of 400,000 tons of flame retardant additives are used worldwide per year in polymer formulations. The main classes of additives are aluminium hydroxide, bromine and chlorine compounds, halogenated and non-halogenated phosphorus compounds, antimony oxides, and boron compounds. The most widely used of these additives, aluminium hydroxide, acts by decomposing endothermically giving off water vapour which cools the burning polymer and restricts oxygen flow to the flame. But aluminium hydroxide is only effective when used at high loadings, so high that the physical and other properties of the polymer may be adversely affected. There is a need for flame retardant combinations which would enable the loading of aluminium hydroxide to be reduced.

The flame-retardant action of chlorine and bromine compounds, either as physically incorporated additives to an organic polymer or as part of the polymer structure itself, is well established. Indeed, halogenated compounds find extensive commercial use as flame retardants, and these are often used in conjunction with synergists such as antimony trioxide and phosphorus derivatives. However, halogen containing polymers generally evolve large amounts of smoke and corrosive gases during combustion, and there is a need for fire retardant formulations which are also smoke-suppressant.

The International Tin Research Institute has been promoting the use of tin compounds as flame retardants. In a recent paper entitled "Investigations into tin-based flame retardants and smoke suppressants", P. A. Cusack and P. I. Fontaine of ITRI reported experiments in which tin compounds replaced antimony trioxide as a

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synergist in halogenated polyester resin formulations. The results showed that the stannates were superior to antimony trioxide, both as flame retardants and as smoke suppressants. In another section, the authors claim that flame-retardant synergism exists between
5 tin compounds and aluminium trihydroxide in (non-halogenated) ethylene-acrylic rubber, but do not provide data to make good their claim.

This invention is based on the discovery
10 that aluminium or magnesium hydroxide and tin oxide or a metal stannate or hydroxystannate form a synergistic flame retardant combination in halogenated polymer formulations. The invention is applicable to all organic polymer formulations, including particularly
15 polyolefins and polyvinylchloride. Where the polymer itself is not halogenated, it is standard practice to include a chlorine or bromine compound, in an amount of from 1 to 30% by weight on the weight of the total formulation. For example, halogenated paraffin waxes
20 are sold for this purpose under the Trademark CERECOLOR.

The term aluminium hydroxide is here used to cover various compounds containing different proportions of Al, O and H, including alpha-aluminium trihydroxide, and alumina hydrate, often wrongly
25 referred to as hydrated aluminium oxides. This component, or alternatively magnesium hydroxide, is used in the formulation at a concentration of 10 to 400 phr (parts per hundred of rubber or parts by weight per hundred parts by weight of the polymer)
30 preferably 50 to 200 phr.

The other component of the flame retardant combination is an oxygen containing tin IV compound. This definition comprises tin oxide or a metal stannate or
35 hydroxystannate. Metal stannates or hydroxystannates of a divalent metal such as Ca, Ba,

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Mg, Bi or particularly Zn, generally have the formula MSnO_3 , M_2SnO_4 or $\text{MSn}(\text{OH})_6$. Tin oxide has the formula SnO_2 , this includes the mono and dihydrated forms. This component is used at a concentration of 0.5 to 80 phr preferably 1 to 25 phr.

As demonstrated below, synergistic effects between the two flame retardant components are observed at a wide range of ratios. In order to keep a desired balance of flame retardant properties, cost and mechanical and other properties of the polymer formulation, it is preferred to use the tin oxide or metal stannate or hydroxystannate in a proportion of 3 to 50% by weight of the aluminium or magnesium hydroxide.

The flame retardant effect of an additive in a polymer formulation can be assessed by measuring the critical oxygen index (COI) by the method of BS 2782: Part 1, Method 1; 1986 (equivalent to ISO 4589-1984). If a combination of additives is used, then it may be predicted that, at a given additive combination loading the COI of the formulation will vary in linear dependence on the relative proportions of the flame retardants in the combination.

Reference is directed to the accompanying drawing, which is a graph of COI against % stannate in a fire retardant additive combination. The polymer is flexible PVC. The additive combination is aluminium hydroxide/zinc stannate (circles) or aluminium hydroxide/zinc hydroxystannate (squares). By comparison of the solid lines (observed) with the dotted lines (predicted on the basis of the above paragraph), a synergistic effect is clearly demonstrated.

The polymer formulations of this invention may contain other conventional ingredients including stabilisers and lubricants and other fire retardants/smoke suppressants. They may be thermoplastic or thermoset. They may be cast, moulded, extruded,

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foamed or treated in any other way which is conventional for polymer formulations. The following example illustrates the invention.

5 A standard PVC formulation was tested both with and without 50 phr aluminium hydroxide. To the filled polymer formulation were added various concentrations of zinc stannate, zinc hydroxystannate and antimony trioxide.

10 The critical oxygen index of each formulation was tested using the above standard procedures. Smoke production was measured in an NBS smoke chamber according to BS 6401: 1983, modified with half inch wire mesh placed in front of the sample to prevent molten sample fouling the furnace. 0.8mm samples were
15 used. Tabulated values indicate "Maximum Specific Optical Density D_m Flaming".

Carbon monoxide CO was measured during combustion in the NBS smoke chamber, using a Telegon continuous carbon monoxide monitor. Results were
20 recorded in p.p.m. 2 minutes after the start of the test.

Example 1

25 The PVC formulation was:

	100 phr	PVC	VY110/51 (K value 66)	Hydro Polymers
	50 phr	Plasticizer	Reomol DOP	Ciba Geigy
30	4 phr	Stabilizer	Irgastab BC26	Ciba Geigy
	0.7 phr	Lubricant	Irgawax 371	Ciba Geigy

Results are set out in the Table below.

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	Composition	COI	Smoke D_m	CO P.P.M.
5				
	No Filler	23.5	371	560
	50phr Aluminium hydroxide	25.6	294	427
	50phr + 6phr $ZnSn(OH)_6$	30.6	280	658
10	50phr + 8phr $ZnSn(OH)_6$	31.4	262	650
	50phr + 10phr $ZnSn(OH)_6$	32.4	242	603
	50phr + 6phr $ZnSnO_3$	31.5	294	720
	50phr + 8phr $ZnSnO_3$	33.0	279	702
15	50phr + 10phr $ZnSnO_3$	34.1	293	645
	50phr + 6phr Sb_2O_3	32.6	388	928
	50phr + 8phr Sb_2O_3	33.4	426	930
	50phr + 10phr Sb_2O_3	34.2	450	937
20				
	6phr $ZnSn(OH)_6$	27.0	354	767
	8phr $ZnSn(OH)_6$	28.5	362	783
	10phr $ZnSn(OH)_6$	28.8	376	784
25				
	6phr $ZnSnO_3$	27.8	373	780
	8phr $ZnSnO_3$	28.8	378	831
	10phr $ZnSnO_3$	29.8	381	855
30				
	6phr Sb_2O_3	30.2	405	768
	8phr Sb_2O_3	30.8	425	890
	10phr Sb_2O_3	31.1	445	1105

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In conjunction with aluminium hydroxide, the zinc stannate and zinc hydroxystannate are seen to have several effects:

- they significantly further increase the COI of the formulation.
- unlike antimony trioxide, they reduce rather than increase smoke generation.
- they result in production of considerably less carbon monoxide than when antimony trioxide is used.

Example 2

Aluminium trihydroxide/calcium hydroxy stannate in flexible PVC.

Formulation

100 phr	PVC	VY110/51	Hydro Polymers
50 phr	Plasticizer	Reomol DOP	Ciba Geigy
4 phr	Stabilizer	Irgastab BC26	Ciba Geigy
0.7 phr	Lubricant	Irgawax 371	Ciba Geigy

Results are set out in the table below.

Phr ATH	Phr $\text{CaSn}(\text{OH})_6$	Critical Oxygen Index
50	0	25.6
45	5	29.5
40	10	30.4
25	25	33.4
0	50	35.6

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Example 3

Magnesium hydroxide/zinc hydroxy stannate in flexible PVC.

5

Formulation

As Example 2 but instead of ATH and calcium hydroxy stnnate:-

10

0-100 phr Magnesium Hydroxide. Flamtard M7 B.A. Chemicals.

0-100 phr $\text{ZnSn}(\text{OH})_6$.

Results

15

	Phr $\text{Mg}(\text{OH})_2$	Phr $\text{ZnSn}(\text{OH})_6$	Critical Oxygen Index
	100	0	27.6
	95	5	34.3
20	90	10	35.5
	50	50	38.7
	0	100	41.4

25

Example 4

Mixtures of aluminium trihydroxide and tin oxide in flexible PVC.

30

Formulation

As Example 2 but instead of ATH and calcium hydroxy stannate:-

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- a. ATH/SnO₂ blends 50 phr.
- b. ATH/SnO₂ blends 100 phr.
- c. ATH/SnO₂ blends 150 phr.

5 Results

	Phr ATH	Phr SnO ₂	Critical Oxygen Index
10			
	50	0	25.6
	40	10	27.9
	32.5	17.5	31.7
	25	25	34.2
15	0	50	34.2
	100	0	29.6
	65	35	34.8
20	50	50	44.0
	0	100	40.2
	150	0	34.8
25	97.5	52.5	48.2
	75	75	55.5
	0	150	45.7

30 Example 5

Mixtures of aluminium trihydroxide and zinc hydroxy stannate in chlorinated rubber.

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Formulation

100	phr	Chlorinated Rubber	Neoprene W	Du Pont
4	phr	Magnesium Oxide	'Light'	BDH
5	0.5	phr	Stearic Acid	
5	phr	Zinc Oxide	'200'	Durham Chemicals
2	phr	Curing Agent	Multisperse E-ETV75P	Croxton and Garry
0-50	phr	ATH	SF7	B A Chemicals
0-50	phr	ZnSn(OH) ₆		
10				

Results

	Phr ATH	Phr ZnSn(OH) ₆	Critical Oxygen Index
15			
	50	0	50.6
	45	5	52.5
	40	10	55.0
	25	25	58.0
20	10	40	55.6
	0	50	51.0

Example 6

25

Mixtures of aluminium hydroxide and zinc hydroxy stannate in unsaturated polyester.

Formulation

30

Unsaturated polyester resin. Synolite R557/44. DSM Resins UK Limited. This resin contains 27% wt of bromine. This was added to the resin as dibromo neopentyl glycol.

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	100	phr	Synolite R557/44	
	2	phr	SA11 $\frac{2}{3}$ Curing Agent	
	1	phr	SC17 $\frac{2}{3}$	
	0-50	phr	ATH FRF60	B A Chemicals
5	0-50	phr	ZnSn(OH) ₆ .	

Results

10	Phr ATH	Phr ZnSn(OH) ₆	Critical Oxygen Index
	50	0	40.6
	48	2	50.1
15	45	5	54.8
	25	25	66.8
	0	50	53.3

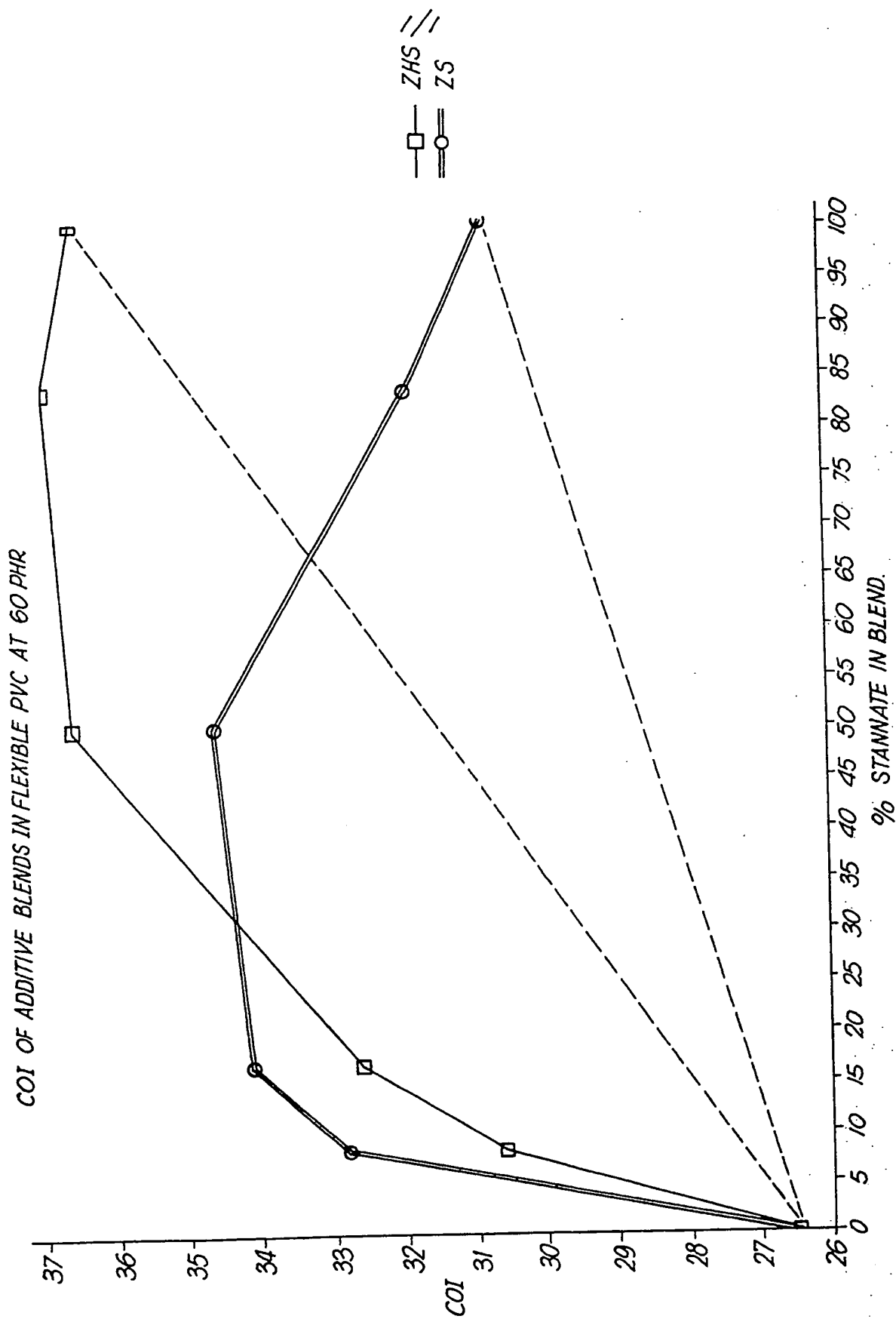
20 If the results for Examples 2 to 6 are
 plotted as a graph of tin oxide or metal
 stannate/hydroxystannate content of the flame
 retardant additive v COI (as in Figure 1) then an
 upwardly convex curve is obtained rather than the
 straight line expected, indicating a synergistic
 25 relationship.

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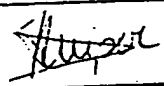
1. A halogenated polymer formulation containing a synergistic flame retardant combination of 10 - 400 phr of an aluminium or magnesium hydroxide and 0.5 - 80 phr of tin oxide or a metal stannate or hydroxystannate.
2. A formulation as claimed in Claim 1, wherein the polymer is polyvinyl chloride.
3. A polymer as claimed in Claim 1 or Claim 2, wherein zinc stannate or hydroxystannate is used.
4. A formulation as claimed in any one of Claims 1 to 3, wherein there is used from 50 - 200 phr of aluminium trihydroxide and from 1 - 25 phr of zinc stannate or hydroxystannate.
5. A formulation as claimed in any one of Claims 1 to 4, wherein the tin oxide or metal stannate or hydroxystannate is used in a proportion of 3 - 50% by weight of aluminium or magnesium hydroxide.



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/01122

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶	
According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ C 08 K 3/18, C 08 L 57/08, 27/06, //(C 08 K 3/18, IPC : 3:22, 3:24)	
II. FIELDS SEARCHED	
Minimum Documentation Searched ⁷	
Classification System ⁸	Classification Symbols
IPC ⁵	C 08 K, C 08 L
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹	
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² Relevant to Claim No. ¹³
A	FR, A, 2436157 (NIPPI INC.) 11 April 1980 see claims 1-3 1
	--
X	Specialty Chemicals, volume 9, no. 3, May/June 1989, P.A. Cusack et al.: "Investigations into tin-based flame retardants and smoke suppressants", pages 194,196, 198,200,202 see page 198, column 2, line 41 - column 3, line 28 1-5

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IV. CERTIFICATION	
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
24th October 1990	14 NOV 1990
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